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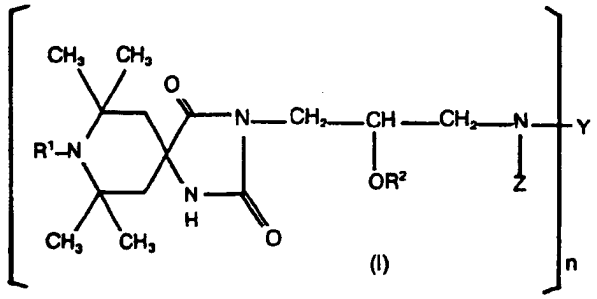
(54) Piperidine-spiro-hydantoin derivatives and their use as light stabilizers for synthetic polymers.

(57) Novel piperidine-spiro-hydantoin derivatives represented by the general formula (I) and use thereof as light stabilizers for synthetic polymers are described:



(I)

The compounds are distinguished by an improved stabilizing effect in various synthetic polymer compositions, such as polyolefins, against light- and/or heat-induced deterioration thereof, low volatility upon heat-processing or during storage of shaped articles containing the compounds, and resistance to extraction with water and solvents.

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or Y and Z may be joined together to form a tetramethylene, pentamethylene, 3-oxapentamethylene, succinyl, glutaryl, maleoyl or phthaloyl group or a group of the formula $-CH_2CH_2\diagdown\!\!\diagup N-R^5$ wherein R^5 is a group of the formula (III), $-CH_2CH_2\diagup\!\!\diagdown$ with the proviso that R^2 and R^4 are hydrogen when Y and/or Z are hydrogen and that R^2 and R^4 are each hydrogen or an acyl group as defined or R^2 is hydrogen and R^4 is an acyl group as defined when Y and Z are both a group of formula (II) or one of Y and Z is a group of the formula (II) and the other is different from hydrogen;

when n is 2,

Y represents an alkylene group having from 2-6 carbon atoms, a phenylene group which may be substituted by methyl, p-xylylene, 1,4-cyclohexylene, the 4,4'-diphenylether or 4,4'-diphenylmethane radical, 2,4-s-triazinediyl, 6-methyl- or 6-phenyl-2,4-s-triazinediyl, and

Z represents a group of the formula (III), 2,2,6,6-tetramethyl-4-piperidyl or 1,2,2,6,6-pentamethyl-4-piperidyl.

In the formula (I),

when n is 1 and

Y and Z represent an alkyl group having from 1 to 18 carbon atoms, they may be, for example, a methyl,ethyl, n-propyl, i-propyl, n-butyl, i-butyl, t-butyl, 2-ethylhexyl, octyl, 2,2,4,4-tetramethylpentyl, decyl, dodecyl, tetradecyl, hexadecyl or octadecyl group, preferably an alkyl group having from 4 to 18 carbon atoms and most preferably an alkyl group having from

8 to 18 carbon atoms;

Y and Z represent an alkenyl group having from 3 to 18 carbon atoms, they may be, for example, an allyl, propenyl, 2-butenyl, 2-pentenyl, 2-hexenyl, 2-octenyl, 5-decenyl, 6-dodecenyl, 7-tetradecenyl, 8-hexadecenyl or 9-octadecenyl group, preferably an allyl or 9-octadecenyl group;

Y and Z represent a cycloalkyl group having from 5 to 7 carbon atoms, they are cyclopentyl, cyclohexyl or cycloheptyl, preferably a cyclohexyl group;

Y and Z represent a phenyl group which may be substituted with a methyl group, they are phenyl or o-, m- or p-tolyl; and when

Y and Z represent an aralkyl group having 7 or 8 carbon atoms, they may be, for example, a benzyl or phenethyl group, preferably a benzyl group.

When n is 2 and

Y represents an alkylene group having from 2 to 6 carbon atoms, it may be, for example, an ethylene, trimethylene or hexamethylene group;

Y represents a phenylene group which may be substituted with a methyl group, it may be, for example, a 1,2-phenylene, 1,3-phenylene, 1,4-phenylene, 2,3-tolylene, 2,4-tolylene or 2,5-tolylene group; or

Y represents a 2,4-s-triazinediyl, 6-methyl- or 6-phenyl-2,4-s-triazinediyl group, preferably a 6-phenyl-2,4-s-triazinediyl group.

When R^2 and/or R^4 represent an acyl group having not more than 18 carbon atoms, they may be, for example, an aliphatic, aromatic, araliphatic or alicyclic acyl group, and the aromatic moiety of said acyl group may be substituted with an alkyl group having from 1 to 4 carbon atoms and/or a hydroxy group, preferably a group of the formula $-COR^6$ wherein R^6 may be an alkyl group having from 1 to 17 carbon atoms; an alkenyl group having 2 or 3 carbon atoms; a phenyl, benzyl or phenethyl group in which the phenyl moiety may be substituted either with one C_{1-4} alkyl group or with two C_{1-4} alkyl groups and one hydroxy group; a styryl group; or a cyclohexyl group. Examples of such acyl groups are the acetyl, propionyl, valeryl, octanoyl, 2-ethylhexanoyl, lauroyl, palmitoyl, stearoyl, acryloyl, crotonoyl, methacryloyl, benzoyl, o-, m- or p-toluoyl, p-tert-butylbenzoyl, 3,5-di-tert-butyl-4-hydroxybenzoyl, phenylacetyl, 3,5-di-tert-butyl-4-hydroxyphenylacetyl, 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionyl, cinnamoyl or cyclohexanecarbonyl group. Particularly preferred acyl groups are alkanoyl groups having not more than 18 carbon atoms,the 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionyl group, or a benzoyl group which may be substituted by an alkyl group having from 1 to 4 carbon atoms.

Compounds of formula (I) wherein R^2 and R^4 are hydrogen atoms are also preferred.

Preferred compounds of formula (I) are those

wherein

1) n represents 1 or 2,

when n is 1, Y and Z are the same or different and represent a hydrogen atom, an alkyl group having from 1-18 carbon atoms, an alkenyl group having from 3-18 carbon atoms, a cycloalkyl group having from 5-7 carbon atoms, an aralkyl group having 7 or 8 carbon atoms, a group of formula (II) or a group of formula (III) with the proviso that, when Y and Z both represent alkyl, alkenyl, cycloalkyl, aralkyl or a group of formula (II) as defined, said groups are identical, and when n is 2, Y represents an alkylene group having from 2-6 carbon atoms, p-xylylene, 2,4-s-triazinediyl, 6-methyl- or 6-phenyl-2,4-s-triazinediyl, and Z represents a group of formula (III). Particularly preferred compounds as defined under 1) are those in which R^2 represents a hydrogen atom.

Particularly preferred compounds of formula (I) are those wherein

2) n is 1, R^2 represents a hydrogen atom, Y represents an alkyl group having from 1-18 carbon atoms, a cycloalkyl or benzyl group, and Z represents a hydrogen atom or a group of formula (III) wherein R^2 is hydrogen.

3) n is 2, Z represents a group of formula (III),

R^2 represents a hydrogen atom, and Y represents an alkylene group having from 2-6 carbon atoms, a p-xylylene group or a 6-phenyl-2,4-s-triazinediyl group.

The most preferred compounds of formula (I) are those in which

4) n is 1, Z represents a group of formula (III), R^2 represents a hydrogen atom, and Y represents an alkyl group having from 1-18 carbon atoms, a cyclohexyl group or a benzyl group, particularly an alkyl group having from 8-18 carbon atoms.

A further class of preferred compounds of formula (I) are those wherein

5) R^2 represents a hydrogen atom,

Z represents a 2,2,6,6-tetramethyl-4-piperidyl or 1,2,2,6,6-pentamethyl-4-piperidyl group, n represents 1 or 2, when n is 1, Y represents an alkyl group having from 1-18 carbon atoms, and, when n is 2, Y represents an alkylene group having from 2-6 carbon atoms, and

6) Y and/or Z represent a group of formula (III) or a group of formula (II), and

R^2 and/or R^4 represent

an alkanoyl group having not more than 18 carbon atoms, a 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionyl group, or a benzoyl group which may be substituted with an alkyl group having from 1-4 carbon atoms.

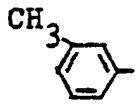
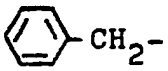
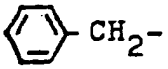
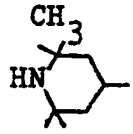
Acid addition salts of compounds of formula (I) are also included in the scope of the present invention. As to the nature of the acid addition salts there is no particular limitation so far as it does not affect the stability of the polymers. Suitable acids for preparing said acid addition salts may be, for example, inorganic acids such as sulfuric acid, hydrochloric acid or phosphoric acid; organic carboxylic acids such as formic acid, acetic acid, valeric acid, stearic acid, oxalic acid, adipic acid, sebacic acid, maleic acid, benzoic acid, p-tert-butylbenzoic acid, 3,5-di-tert-butyl-4-hydroxbenzoic acid, salicylic acid or terephthalic acid; organic sulfonic acids such as methanesulfonic acid or p-toluenesulfonic acid; or organic phosphonic acids such as phenylphosphonic acid.

Below a non-limiting list of specific piperidine-spirohydantoin derivatives of formula (I) is given. The numbering of the compounds is the same as in the Examples.

<u>when n is 1</u>

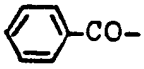
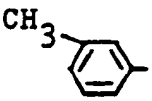
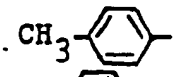
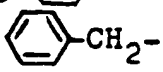
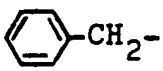
a) compounds in which Z is a hydrogen atom

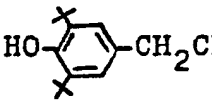
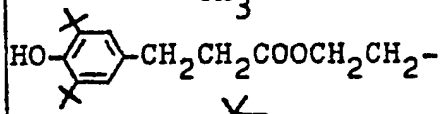
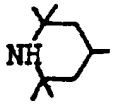
Compound No.	R^1	R^2	Y
a - 1	H	H	H
2	CH_3	H	H
3	H	H	$n\text{-}C_3H_7$-
4	CH_3	H	$i\text{-}C_3H_7$-
5	CH_3	H	$n\text{-}C_4H_9$-
6	CH_3	H	$t\text{-}C_4H_9$-
7	CH_3	H	$CH_3(CH_2)_3CHCH_2$- (with C_2H_5 branch)
8	CH_3	H	$n\text{-}C_8H_{17}$-
9	H	H	$n\text{-}C_{10}H_{21}$-
10	CH_3	H	$n\text{-}C_{10}H_{21}$-
11	H	H	$n\text{-}C_{12}H_{25}$-
12	CH_3	H	$n\text{-}C_{12}H_{25}$-
13	CH_3	H	$n\text{-}C_{14}H_{29}$-
14	H	H	$n\text{-}C_{16}H_{33}$-
15	CH_3	H	$n\text{-}C_{16}H_{33}$-
16	H	H	$n\text{-}C_{18}H_{37}$-
17	CH_3	H	$n\text{-}C_{18}H_{37}$-
18	CH_3	H	$CH_2=CH\text{-}CH_2$-
19	H	H	$CH_3(CH_2)_7CH=CH(CH_2)_8$-
20	H	H	
21	CH_3	H	
22	CH_3	H	

23	H	H	
24	H	H	
25	CH_3	H	
26	H	H	$HOCH_2CH_2-$
27	CH_3	H	$HOCH_2CH_2-$
28	H	H	$HOCH(CH_3)-CH_2-$
29	CH_3	H	$HOCH(CH_3)-CH_2-$
30	CH_3	H	

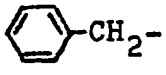
b) compounds in which Z is a group of formula (III)

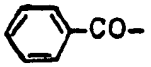
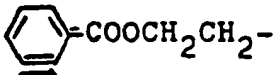
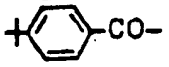
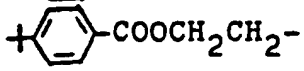
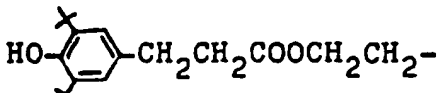
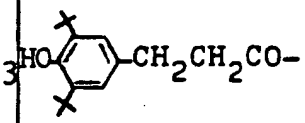
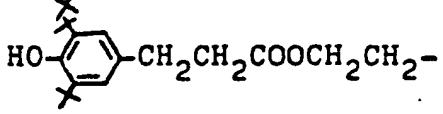
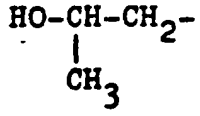
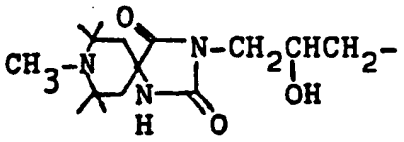
Compound No.	R^1	R^2	Y
b - 1	H	H	H
2	CH_3	H	H
3	H	H	CH_3-
4	CH_3	H	$n\text{-}C_3H_7-$
5	CH_3	H	$i\text{-}C_3H_7-$
6	H	H	$n\text{-}C_4H_9-$
7	CH_3	H	$n\text{-}C_4H_9-$
8	H	H	$CH_3(CH_2)_3CH(C_2H_5)CH_2-$
9	CH_3	H	$n\text{-}C_8H_{17}-$

10	H	H	$n\text{-}C_{10}H_{21}$-
11	CH_3	H	$n\text{-}C_{10}H_{21}$-
12	H	H	$n\text{-}C_{12}H_{25}$-
13	CH_3	H	$n\text{-}C_{12}H_{25}$-
14	H		$n\text{-}C_{12}H_{25}$-
15	H	H	$n\text{-}C_{14}H_{29}$-
16	CH_3	H	$n\text{-}C_{14}H_{29}$-
17	H	H	$n\text{-}C_{16}H_{33}$-
18	CH_3	H	$n\text{-}C_{16}H_{33}$-
19	H	H	$n\text{-}C_{18}H_{37}$-
20	CH_3	H	$n\text{-}C_{18}H_{37}$-
21	CH_3	CH_3CO-	$n\text{-}C_{18}H_{37}$-
22	CH_3	H	$CH_2{=}CH\text{-}CH_2$-
23	H	H	$CH_3(CH_2)_7CH{=}CH(CH_2)_8$-
24	H	H	
25	H	H	
26	CH_3	H	
27	H	H	
28	CH_3	H	
29	H	H	
30	H	H	
31	CH_3	H	
32	H	H	$HOCH_2CH_2$-
33	CH_3	H	$HOCH_2CH_2$-

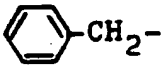
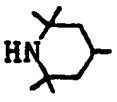
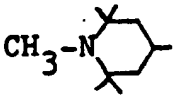
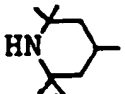
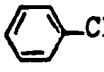
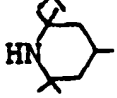
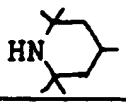
34	H	n-C_4H_9CO-	n-$C_4H_9COOCH_2CH_2$-
35	CH_3	n-$C_{11}H_{23}CO$-	n-$C_{11}H_{23}COOCH_2CH_2$-
36	CH_3	H	$HOCHCH_2$- (with CH_3 branch)
37	CH_3		
38	H	H	

c) compounds in which Z is the same group as Y

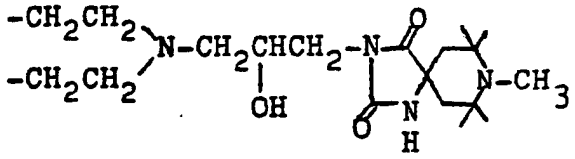
Compound No.	R^1	R^2	Z,Y
c - 1	CH_3	H	C_2H_5-
2	CH_3	CH_3CO-	i-C_3H_7-
3	H	H	n-C_8H_{17}-
4	CH_3	H	n-$C_{10}H_{21}$-
5	H	H	n-$C_{12}H_{25}$-
6	CH_3	H	$CH_3(CH_2)_7CH{=}CH(CH_2)_8$-
7	CH_3	H	
8	H	H	
9	CH_3	H	
10	H	H	$HOCH_2CH_2$-
11	CH_3	H	$HOCH_2CH_2$-
12	CH_3	H	n-$C_4H_9COOCH_2CH_2$-
13	CH_3	n-$C_{11}H_{23}CO$-	n-$C_{11}H_{23}COOCH_2CH_2$-
14	CH_3	H	n-$C_{17}H_{35}COOCH_2CH_2$-

15	CH_3		
16	CH_3		
17	CH_3	H	
18	CH_3		
19	CH_3	H	
20	CH_3	H	

d) compounds in which Z and Y are different groups

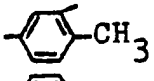
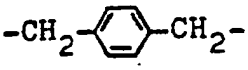
Compound No.	R^1	R^2	Y	Z
d - 1	CH_3	H	C_2H_5-	n-C_4H_9-
2	CH_3	H	CH_3-	
3	H	H	CH_3-	
4	CH_3	H	n-C_4H_9-	
5	CH_3	H	n-C_8H_{17}-	
6	H	H	n-$C_{12}H_{25}$-	
7	H	H		
8	H	H	$HOCH_2CH_2$-	

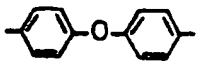
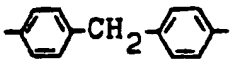
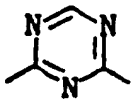
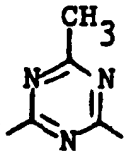
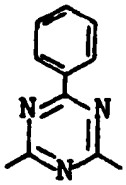
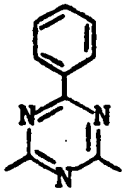
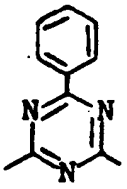
e) compounds in which Y and Z are joined together to form a group

Compound No.	R^1	R^2	Y + Z
e - 1	CH_3	H	$-(CH_2)_5-$
2	CH_3	H	$-(CH_2)_2-O-(CH_2)_2-$
3	CH_3	H	$-CO-(CH_2)_2-CO-$
4	H	H	
5	CH_3	H	

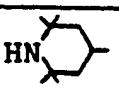
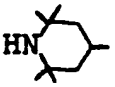
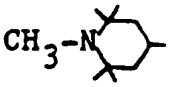
when n is 2

f) compounds in which Z is a group of formula (III)

Compound No.	R^1	R^2	Y
f - 1	H	H	$-(CH_2)_2-$
2	H	H	$-(CH_2)_6-$
3	CH_3	H	$-(CH_2)_6-$
4	CH_3	H	
5	H	H	
6	CH_3	H	

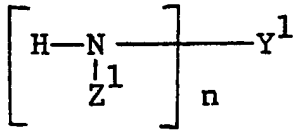
7	CH_3	H	
8	CH_3	H	
9	CH_3	H	
10	CH_3	H	
11	CH_3	H	
12	H	H	
13	CH_3	H	
14	CH_3	CH_3CO-	

g) compounds in which Z is a group different from that of formula (III)

Compound No.	R^1	R^2	Y	Z
g - 1	H	H	$-(CH_2)_2-$	
2	H	H	$-(CH_2)_6-$	
3	CH_3	H	$-(CH_2)_6-$	

The piperidine-spiro-hydantoin derivatives of formula (I) of the present invention may be prepared by reacting an amino derivative with the requisite amount of a 3-(2,3-epoxypropyl)-piperidine-spiro-hydantoin derivative and, if desired, by acylating the resultant product.

More particularly, the compounds of formula (I) may be prepared by reacting a compound of the formula



(IV)

wherein

n represents 1 or 2,

when n is 1, Y^1 and Z^1 may be the same or different and represent a hydrogen atom, a C_{1-18} alkyl, a C_{3-18} alkenyl or a C_{5-7} cycloalkyl group, a phenyl group which may be substituted with a methyl group, a C_{7-8} aralkyl group, a group of the formula $-CH_2-\underset{R^3}{CH}-OH$ wherein R^3 has the same meaning as defined above, a 2,2,6,6-tetramethyl-4-piperidyl or 1,2,2,6,6-pentamethyl-4-piperidyl group, or

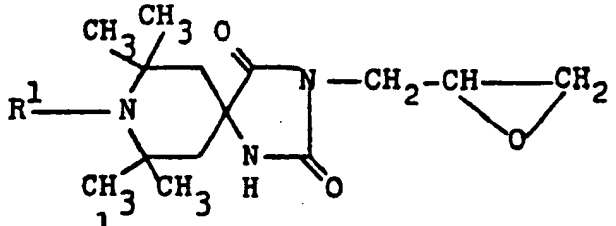
Y^1 and Z^1 may jointly together represent a tetramethylene, pentamethylene, 3-oxapentamethylene, succinyl, glutaryl, maleoyl or phthaloyl group, or $-CH_2CH_2\diagdown\diagup NH$;
$-CH_2CH_2\diagup$

when n is 2, Y^1 represents a C_{2-6} alkylene group, a phenylene group which may be substituted with a methyl group, a p-xylylene group, a 1,4-cyclohexylene group, a 4,4'-diphenylether radical, a 4,4'-diphenylmethane radical, a

2,4-s-triazinediyl group, a 6-methyl-2,4-s-triazinediyl group or a 6-phenyl-2,4-s-triazinediyl group;

Z^1 represents a hydrogen atom, a 2,2,6,6-tetramethyl-4-piperidyl or 1,2,2,6,6-pentamethyl-4-piperidyl group,

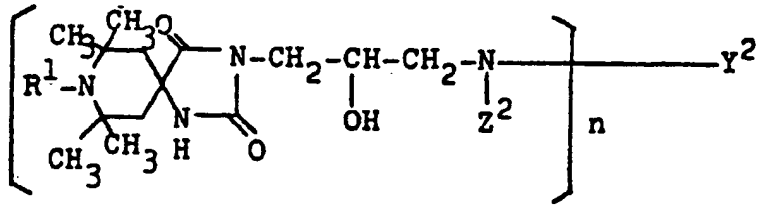
with an appropriate amount of a compound of the formula



(V)

wherein R^1 has the same meaning as defined above,

to prepare a compound of the formula



(VI)

wherein n represents 1 or 2,

when n is 1, Y^2 and Z^2 may be the same or different and represent a hydrogen atom, a C_{1-18} alkyl, a C_{3-18} alkenyl or a C_{5-7} cycloalkyl group, a phenyl group which may be substituted with a methyl group, a C_7 or C_8 aralkyl group, a group of the formula $-CH_2-\underset{R^3}{CH}-OH$ wherein R^3 has the same meaning as defined above, a 2,2,6,6-tetramethyl-4-piperidyl or 1,2,2,6,6-pentamethyl-4-piperidyl group or a group of formula (III) in which R^2 is a hydrogen atom, or

Y^2 and Z^2 may jointly represent a tetramethylene, pentamethylene, 3-oxapentamethylene, succinyl, glutaryl,

maleoyl or phthaloyl group, or a group of the formula $-CH_2CH_2$ / $-CH_2CH_2$ >N-$R^{5'}$ wherein $R^{5'}$ represents a group of formula (III) in which R^2 is a hydrogen atom,

when n is 2, Y^2 represents a C_{2-6} alkylene group, a phenylene group which may be substituted with a methyl group, a p-xylylene group, a 1,4-cyclohexylene group, a 4,4'-diphenylether radical, a 4,4'-diphenylmethane radical, a 2,4-s-triazinediyl group, a 6-methyl-2,4-s-triazinediyl group or a 6-phenyl-2,4-s-triazinediyl group,

Z^2 represents a 2,2,6,6-tetramethyl-4-piperidyl or 1,2,2-6,6-pentamethyl-4-piperidyl group or a group of formula (III) in which R^2 is a hydrogen atom,

and, if desired, by subsequently acylating the product in a manner known per se.

In preparing compounds of the above-described formula (VI), the amount of compound of formula (V) required depends upon the number of groups of formula (III), wherein R^2 is a hydrogen atom, to be introduced into the compound of formula (IV).

The reaction is suitably carried out by heating a mixture of the amino derivative of the above-described formula (IV) and an appropriate amount of the compound of formula (V) at from room temperature to 200°C, preferably at from 50 to 150°C in the presence or absence of an inert organic solvent. As to the solvent there is no particular

limitation so far as it is indifferent to the reaction, and there may be employed, for example, water; an ether such as dioxane, diethylene glycol, dimethyl ether or the like; a dialkyl amide such as dimethyl formamide, dimethyl acetamide or the like; an aliphatic hydrocarbon such as n-hexane, n-heptane or the like; a chlorinated or non-chlorinated aromatic hydrocarbon such as benzene, toluene, xylene, chlorobenzene, p-dichlorobenzene or the like; an alcohol such as anhydrous or hydrous methanol, ethanol, n- or t-butanol or the like. Preferably aromatic hydrocarbons and anhydrous or hydrous alcohols are used; anhydrous or hydrous alcohols are particularly preferred. The reaction is advantageously carried out in the presence of a basic alkali metal compound such as sodium hydroxide, potassium hydroxide, potassium carbonate or the like.

When the compound of formula (VI) is to be acylated, the reaction is carried out by reacting the compound of formula (VI) with a reactive derivative of a carboxylic acid (acid halide, acid anhydride or acid lower alkyl ester) corresponding to the acyl group to be introduced. The acylating agent may be suitably selected depending upon the type of acyl group to be introduced; use of an acid lower alkyl ester is particularly preferred. The amount of acylating agent to be employed may vary depending upon the number of acyl groups to be introduced.

When an acid ester is employed, the reaction is con-

veniently carried out in an inert organic solvent in the presence of a strong base. As preferred solvent there may be used, for example, an aromatic or aliphatic hydrocarbon such as benzene, toluene, xylene, n-heptane, n-octane, i-octane or the like. As suitable strong base there may be used, for example, a strongly basic alkali metal compound such as sodium methylate, sodium ethylate, potassium hydroxide, lithium amide or the like, or a titanic acid derivative such as tetraisopropyl titanate or tetrabutyl titanate. The reaction proceeds conveniently by heating usually at 80-180°C.

When an acid halide is employed, the reaction is conveniently carried out in an inert organic solvent in the presence of an acid-binding agent. As solvent there may be preferably used, for example, an aromatic hydrocarbon such as benzene, toluene, xylene or the like; a halogenated aliphatic hydrocarbon such as chloroform, trichloroethane or the like; or an ether such as diethyl ether, tetrahydrofuran, dioxane or the like. As acid-binding agent there may be preferably used, for example, an alkali metal hydroxide such as sodium hydroxide, potassium hydroxide or the like; an alkali metal carbonate such as sodium carbonate, potassium carbonate or the like; or an organic base such as triethylamine, pyridine or the like. The reaction is usually carried out at 0-130°C.

When an acid anhydride is employed, the reaction is carried out in the presence of an inert organic solvent

or in the absence of an inert organic solvent using an excess of acid anhydride. As solvent there may be preferably used, for example, an aromatic hydrocarbon such as benzene, toluene, xylene or the like; or an ether such as dioxane, tetrahydrofuran, diethylene glycol, dimethyl ether or the like. The reaction is usually carried out at from room temperature to 160°C.

The piperidine-spiro-hydantoin derivatives of formula (I) and their acid addition salts according to the present invention exhibit a low heat-volatility as well as a low migration property; they are effective stabilizers against the light- and heat-induced deterioration of a wide variety of synthetic polymers.The following may be mentioned as polymers which can be stabilized by these compounds:

olefin and diene polymers

including homopolymers of olefins and dienes (e.g. low-density, high-density and cross-linked polyethylenes, polypropylene, polyisobutylene, polymethylbutene-1, polymethylpentene-1, polyisoprene and polybutadiene), mixtures of such homopolymers (e.g. mixtures of polypropylene and polyethylene, polypropylene and polybutene-1, or polypropylene and polyisobutylene), and copolymers of olefins and dienes (e.g. ethylene/propylene copolymers,propylene/butene-1 copolymers,propylene/isobutene copolymers,ethylene/butene-1 copolymers and terpolymers of ethylene and propylene with dienes such as hexadiene, dicyclopentadiene or ethylidene norbornene);

styrene polymers

including polystyrene, copolymers of styrene and of α-methylstyrene (e.g. styrene/butadiene copolymers, styrene/acrylonitrile copolymers, styrene/acrylonitrile/methyl methacrylate copolymers, styrene/acrylonitrile/acrylic ester copolymers, styrene/acrylonitrile copolymers modified with acrylic ester polymers to provide impact strength, and styrene polymers modified with EPDM to provide impact strength), and graft copolymers of styrene (e.g. polymers in which styrene is grafted onto polybutadiene, and polymers in which styrene and acrylonitrile are grafted onto polybutadiene usually called acrylonitrile/butadiene/styrene or ABS plastics);

halogenated vinyl and vinylidene polymers

including polyvinyl chloride, polyvinylidene chloride, polyvinyl fluoride, polychloroprene, chlorinated rubbers, vinyl chloride/vinylidene chloride copolymers, vinyl chloride/vinyl acetate copolymers, and vinylidene chloride/vinyl acetate copolymers;

polymers derived from α,β-unsaturated acids

and derivatives thereof, including polyacrylates and polymethacrylates, polyacrylamides and polyacrylonitrile;

polymers derived from unsaturated alcohols and amines

and from the acyl derivatives thereof or acetals, including polyvinyl alcohol, polyvinyl acetate, polyvinyl stearate, polyvinyl benzoate, polyvinyl maleate, polyvinyl butyral,

polyallyl phthalate, and polyallyl melamine, and copolymers thereof with other ethylenically unsaturated monomers (e.g. ethylene/vinyl acetate copolymers);

epoxy polymers

including homopolymers and copolymers derived from epoxides (e.g. polyethylene oxide) and polymers derived from bis-glycidyl ethers;

polyacetals, polyalkylene oxides and polyphenylene oxides

including polyoxymethylene, oxymethylene/ethylene oxide copolymers, polyoxyethylene, polypropylene oxide, poly-isobutylene oxide and polyphenylene oxides;

polyurethanes and polyureas;

polycarbonates;

polysulfones;

polyamides and copolyamides

derived from diamines and aliphatic or aromatic dicarboxylic acids and/or from aminocarboxylic acids or the corresponding lactams, including nylon-6, nylon-6/6, nylon-6/10, nylon-11 and nylon-12;

polyesters

derived from dicarboxylic acids and dialcohols and/or from hydroxycarboxylic acids and the corresponding lactones, including polyethylene glycol terephthalate and poly-1,4-dimethylol-cyclohexane terephthalate;

cross-linked polymers

derived from aldehydes together with phenols, ureas, or melamines, e.g. phenol/formaldehyde, urea/formaldehyde and melamine/formaldehyde resins;

alkyd resins

including glycerol-phthalic acid resins and mixtures thereof with melamine/formaldehyde resins; and

unsaturated polyester resins

derived from copolyesters of saturated and unsaturated dicarboxylic acids with polyhydric alcohols as well as from vinyl compounds as cross-linking agents, and also halogenated flame-resistant modifications thereof.

The amount of stabilizer of formula (I) needed for an effective stabilization of the polymers will depend on a variety of factors, such as the type and property of the polymers concerned, their intended use, and the presence of other stabilizers. It is generally satisfactory to use from 0.01 to 5.0% by weight of a stabilizer of formula (I), based on the weight of the polymer, but the most effective range will vary with the type of polymer: viz. 0.01 to 2.0%, preferably 0.02 to 1.0%, by weight for olefin, diene and styrene polymers; 0.01 to 1.0%, preferably 0.02 to 0.5%, by weight for vinyl chloride and vinylidene chloride polymers; and 0.01 to 5.0%, preferably 0.02 to 2.0%, by weight for polyurethanes and polyamides. If desired, two or more of the stabilizers of formula (I) may be used

together.

The stabilizers of the invention may readily be incorporated into polymers by conventional techniques at any convenient stage prior to the manufacture of shaped articles therefrom. For example, the stabilizer may be mixed with the polymer in dry powder form, or a suspension or emulsion of the stabilizer may be mixed with a solution, suspension or emulsion of the polymer.

The stabilized polymeric composition of the invention may optionally contain various additives conventionally used in polymer technology, such as the additives listed in British Patent Specification No. 1 401 924, at pages 11-13.

The invention is further illustrated by the following Examples, in which all parts and percentages are by weight.

Example 1. N,N-Bis[2-hydroxy-3-(7,7,8,9,9-pentamethyl-2,4-dioxo-1,3,8-triazaspiro[4.5]dec-3-yl)propyl]decylamine (Compound No. b-11)

To a solution of 3.0 g of 7,7,8,9,9-pentamethyl-3-(2,3-epoxypropyl)-2,4-dioxo-1,3,8-triazaspiro[4.5]decane and 0.8 g of decylamine in 100 ml of methanol was added 0.1 g of potassium hydroxide, and the mixture was heated under reflux for 8 hours. After completion of the reaction, the mixture was condensed to a volume of 50 ml and allowed to stand at room temperature. The crystals precipitated were collected by filtration, washed with a small amount of methanol, dried under reduced pressure,

and recrystallized from benzene to afford the desired compound as white crystals of m.p. 180°C.

Example 2. N,N-Bis[2-hydroxy-3-(7,7,8,9,9-pentamethyl-2,4-dioxo-1,3,8-triazaspiro[4.5]dec-3-yl)propyl]butylamine (Compound No. b-7)

Using 3.0 g of 7,7,8,9,9-pentamethyl-3-(2,3-epoxypropyl)-2,4-dioxo-1,3,8-triazaspiro[4.5]decane and 0.36 g of butylamine, the reaction and the post-treatment were carried out according to the same procedure as in Example 1. The crude crystals thus obtained were recrystallized from toluene to afford the desired compound as white crystals of m.p. 178°C.

Example 3. N-(2,2,6,6-Tetramethyl-4-piperidyl)-N-[2-hydroxy-3-(7,7,8,9,9-pentamethyl-2,4-dioxo-1,3,8-triazaspiro[4.5]-dec-3-yl)propyl]butylamine (Compound No. d-4)

Using 3.0 g of 7,7,8,9,9-pentamethyl-3-(2,3-epoxypropyl)-2,4-dioxo-1,3,8-triazaspiro[4.5]decane and 2.1 g of 2,2,6,6-tetramethyl-4-butylaminopiperidine, the reaction and the post-treatment were carried out according to the same procedure as in Example 1. The crude crystals thus obtained were recrystallized from benzene to afford the desired compound as white crystals of m.p. 74-76°C.

Example 4. 3-[3-Di(2-hydroxyethyl)amino-2-hydroxypropyl]-7,7,8,9,9-pentamethyl-2,4-dioxo-1,3,8-triazaspiro[4.5]decane

(Compound No. c-11)

Using 3.0 g of 7,7,8,9,9-pentamethyl-3-(2,3-epoxypropyl)-2,4-dioxo-1,3,8-triazaspiro[4.5]decane and 1.1 g of diethanolamine, the reaction and the post-treatment were carried out according to the same procedure as in Example 1. The crude crystals thus obtained were recrystallized from benzene to afford the desired compound as white crystals of m.p. 155-156°C.

Example 5. N,N,N',N'-Tetra[2-hydroxy-3-(7,7,8,9,9-pentamethyl-2,4-dioxo-1,3,8-triazaspiro[4.5]dec-3-yl)propyl]-hexamethylenediamine

(Compound No. f-3)

Using 3.0 g of 7,7,8,9,9-pentamethyl-3-(2,3-epoxypropyl)-2,4-dioxo-1,3,8-triazaspiro[4.5]decane and 0.25 g of hexamethylenediamine, the reaction and the post-treatment were carried out according to the same procedure as in Example 1. The crude crystals thus obtained were recrystallized from ethanol to afford the desired compound as white crystals of m.p. 274-275°C.

Example 6. N,N,N',N'-Tetra[2-hydroxy-3-(7,7,8,9,9-pentamethyl-2,4-dioxo-1,3,8-triazaspiro[4.5]dec-3-yl)propyl]-p-xylenediamine

(Compound No. f-6)

Using 3.0 g of 7,7,8,9,9-pentamethyl-3-(2,3-epoxypropyl)-2,4-dioxo-1,3,8-triazaspiro[4.5]decane and 0.3 g of p-xylenediamine, the reaction and the post-treatment were

carried out according to the same procedure as in Example 1. The crude crystals thus obtained were recrystallized from benzene to afford the desired compound as white crystals of m.p. 128-131°C.

Example 7. 3-(3-Diethylamino-2-hydroxypropyl)-7,7,8,9,9-pentamethyl-2,4-dioxo-1,3,8-triazaspiro[4.5]decane (Compound No. c-1)

Using 3.0 g of 7,7,8,9,9-pentamethyl-3-(2,3-epoxypropyl)-2,4-dioxo-1,3,8-triazaspiro[4.5]decane and 0.7 g of diethylamine, the reaction was carried out according to the same procedure as in Example 1. After completion of the reaction, methanol was removed by distillation and the residue was dissolved in ethyl acetate. The solution was washed with water, dried over sodium sulfate, and ethyl acetate was evaporated to give crude crystals, which were recrystallized from ethyl acetate to give the desired compound as white crystals of m.p. 140-143°C.

Example 8. 3-(3-Cyclohexylamino-2-hydroxypropyl)-7,7,8,9,9-pentamethyl-2,4-dioxo-1,3,8-triazaspiro[4.5]decane (Compound No. a-21)

To a solution of 3.0 g of 7,7,8,9,9-pentamethyl-3-(2,3-epoxypropyl)-2,4-dioxo-1,3,8-triazaspiro[4.5]decane and 1.0 g of cyclohexylamine in 100 ml of methanol was added 0.1 g of potassium hydroxide, and the mixture was heated under reflux for 18 hours. After completion of the reaction, the mixture was filtered and the solvent was

evaporated from the filtrate. The residue was dissolved in ethyl acetate, the solution washed with water, dried over sodium sulfate, and the solvent was removed by distillation. The crude crystals thus obtained were purified by column chromatography through silica gel, using a mixture of ethyl acetate and methanol (2 : 1) as the first eluent and methanol as the second eluent to afford the desired compound as white crystals of m.p. 159-163°C.

Example 9. N,N-Bis[2-hydroxy-3-(7,7,8,9,9-pentamethyl-2,4-dioxo-1,3,8-triazaspiro[4.5]dec-3-yl)propyl]benzylamine (Compound No. b-31)

To a solution of 5.9 g of 7,7,8,9,9-pentamethyl-3-(2,3-epoxypropyl)-2,4-dioxo-1,3,8-triazaspiro[4.5]decane and 1.1 g of benzylamine in 100 ml of methanol was added 0.1 g of potassium hydroxide, and the mixture was heated under reflux for 12 hours. After completion of the reaction, the mixture was treated according to the same procedure as in Example 8 and the crude crystals thus obtained were purified by column chromatography through silica gel using a mixture of benzene and ethyl acetate (1 : 1) as the first eluent and a mixture of ethyl acetate and methanol (1 : 1) as the second eluent to afford the desired compound as white crystals of m.p. 86-96°C.

Example 10. N,N,N',N'-Tetra[2-hydroxy-3-(7,7,8,9,9-pentamethyl-2,4-dioxo-1,3,8-triazaspiro[4.5]dec-3-yl)propyl]-2,4-diamino-6-phenyl-1,3,5-triazine

(Compound No. f-13)

A mixture of 3.0 g of 7,7,8,9,9-pentamethyl-3-(2,3-epoxypropyl)-2,4-dioxo-1,3,8-triazaspiro[4.5]decane and 0.44 g of benzoguanamine was heated at 170-180°C for 4 hours. After completion of the reaction, the mixture was crystallized from benzene to afford the desired compound as pale yellow crystals of m.p. 145-154°C.

Example 11. N,N-Bis[2-hydroxy-3-(7,7,8,9,9-pentamethyl-2,4-dioxo-1,3,8-triazaspiro[4.5]dec-3-yl)propyl]cyclohexylamine

(Compound No. b-26)

A mixture of 5.9 g of 7,7,8,9,9-pentamethyl-3-(2,3-epoxypropyl)-2,4-dioxo-1,3,8-triazaspiro[4.5]decane and 1.0 g of cyclohexylamine was heated at 140°C for 30 minutes. After completion of the reaction, the mixture was dissolved in hot dichloroethane, the solution filtered, and the solvent was evaporated from the filtrate to give crude crystals, which were washed with ethyl acetate and dried under reduced pressure to afford the desired compound as white crystals of m.p. 230-235°C.

Example 12. N,N-Bis[2-hydroxy-3-(7,7,8,9,9-pentamethyl-2,4-dioxo-1,3,8-triazaspiro[4.5]dec-3-yl)propyl]octadecylamine

(Compound No. b-20)

A mixture of 5.9 g of 7,7,8,9,9-pentamethyl-3-(2,3-epoxypropyl)-2,4-dioxo-1,3,8-triazaspiro[4.5]decane and 2.7 g of octadecylamine was heated at 180°C for 24 hours.

After completion of the reaction, the mixture was crystallized from ethyl acetate to afford the desired compound as white crystals of m.p. 166-171°C.

Example 13. N,N-Bis[2-hydroxy-3-(7,7,9,9-tetramethyl-2,4-dioxo-1,3,8-triazaspiro[4.5]dec-3-yl)propyl]octadecylamine (Compound No. b-19)

Using 1.2 g of 7,7,9,9-tetramethyl-3-(2,3-epoxypropyl)-2,4-dioxo-1,3,8-triazaspiro[4.5]decane and 0.54 g of octadecylamine, the reaction and the post-treatment were carried out according to the same procedure as in Example 9 to afford the desired compound as white crystals of m.p. 56-58°C.

Example 14. N,N-Bis[2-hydroxy-3-(7,7,9,9-tetramethyl-2,4-dioxo-1,3,8-triazaspiro[4.5]dec-3-yl)propyl]benzylamine (Compound No. b-30)

To a solution of 1.4 g of 7,7,9,9-tetramethyl-3-(2,3-epoxypropyl)-2,4-dioxo-1,3,8-triazaspiro[4.5]decane and 0.27 g of benzylamine in 10 ml of methanol was added 0.05 g of potassium hydroxide, and the mixture was heated under reflux for 9 hours. After completion of the reaction, the solvent was removed by distillation from the reaction mixture and the residue was dissolved in chloroform. The solution was washed with water, dried over sodium sulfate, the solvent was evaporated under reduced pressure to afford the desired compound as white crystals of m.p. 180-185°C.

Example 15. 3-[3-Di{2-(4-tert-butylbenzoyloxy)ethyl}amino-2-{4-tert-butylbenzoyloxy}propyl]-7,7,8,9,9-pentamethyl-2,4-dioxo-1,3,8-triazaspiro[4.5]decane (Compound No. c-16)

In 250 ml of xylene were dissolved 2.9 g of 3-[3-di(2-hydroxyethyl)amino-2-hydroxypropyl]-7,7,8,9,9-pentamethyl-2,4-dioxo-1,3,8-triazaspiro[4.5]decane prepared in Example 4 and 6.0 g of methyl 4-tert-butylbenzoate, and 0.5 g of lithium amide was added to the solution. The mixture was heated under reflux for 8 hours and methanol formed was removed by distillation little by little together with xylene, while keeping the volume of the reaction mixture constant by adding xylene in an amount to compensate the volume of the distilled methanol and xylene. After completion of the reaction, the mixture was washed with water, dried over sodium sulfate, and the solvent was evaporated to give crude crystals which were recrystallized from n-hexane to afford the desired compound as white crystals of m.p. 180-181°C.

Example 16. 3-[3-Di{2-(3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionyloxy)ethyl}amino-2-hydroxypropyl]-7,7,8,9,9-pentamethyl-2,4-dioxo-1,3,8-triazaspiro[4.5]decane (Compound No. c-17)

Using 2.0 g of 3-[3-di(2-hydroxyethyl)amino-2-hydroxypropyl]-7,7,8,9,9-pentamethyl-2,4-dioxo-1,3,8-triazaspiro[4.5]decane prepared in Example 4 and 3.0 g of methyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate, the reaction

and the post-treatment were carried out according to the same procedure as in Example 15 to give a viscous oily substance, which was purified by column chromatography through silica gel using ethyl acetate as the eluent to afford the desired compound as a pale yellow viscous oily substance. The compound exhibited an Rf value of 0.55 in the silica gel thin layer chromatography using ethyl acetate as the developing solvent.

Example 17. 3-[3-Di(2-lauroyloxyethyl)amino-2-lauroyloxypropyl]-7,7,8,9,9-pentamethyl-2,4-dioxo-1,3,8-triazaspiro-[4.5]-decane

(Compound No. c-13)

Using 3.0 g of 3-[3-di(2-hydroxyethyl)amino-2-hydroxypropyl]-7,7,8,9,9-pentamethyl-2,4-dioxo-1,3,8-triazaspiro-[4.5]decane prepared in Example 4 and 4.9 g of methyl laurate, the reaction and the post-treatment were carried out according to the same procedures as in Example 16 to afford the desired compound as a colorless viscous oily substance. The compound showed an Rf value of 0.50 in the silica gel thin layer chromatography using ethyl acetate as the developing solvent.

Example 18. N,N,N',N'-Tetra[2-acetoxy-3-(7,7,8,9,9-pentamethyl-2,4-dioxo-1,3,8-triazaspiro[4.5]dec-3-yl)propyl]-2,4-diamino-6-phenyl-1,3,5-triazine

(Compound No. f-14)

A solution of 2.0 g of N,N,N',N'-tetra[2-hydroxy-3-(7,

7,8,9,9-pentamethyl-2,4-dioxo-1,3,8-triazaspiro[4.5] dec-3-yl)propyl]-2,4-diamino-6-phenyl-1,3,5-triazine prepared in Example 10 in 50 ml of acetic anhydride was heated at 100°C for 5 hours. After completion of the reaction, residual unreacted acetic acid and acetic anhydride were removed by distillation from the reaction mixture. After addition of benzene to the residue, the mixture was washed with an aqueous 3% sodium carbonate solution and water, successively, dried over magnesium sulfate, and the solvent was evaporated to give crude crystals. Recrystallization of the crude crystals from benzene afforded the desired compound as pale yellow crystals of m.p. 166-174°C.

Example 19. 3-(2-Hydroxy-3-tert-butylaminopropyl)-7,7,8,9,9-pentamethyl-2,4-dioxo-1,3,8-triazaspiro[4.5]decane (Compound No. a-6)

In a mixture of 15 ml of tetrahydrofuran and 20 ml of dimethylformamide were dissolved 10 g of 7,7,8,9,9-pentamethyl-3-(2,3-epoxypropyl)-2,4-dioxo-1,3,8-triazaspiro[4.5]-decane and 2.5 g of tert-butylamine and the solution was heated under reflux for 16 hours. After completion of the reaction, the mixture was poured into 25 ml of water, the precipitated crystals were collected by filtration, washed with water and dried by heating under reduced pressure. The crude crystals thus obtained were recrystallized from ethyl acetate to afford the desired compound as white crystals of m.p. 177.0-177.5°C.

Example 20. N,N,-Bis[2-hydroxy-3-(7,7,8,9,9-pentamethyl-2,4-dioxo-1,3,8-triazaspiro[4.5]dec-3-yl)propyl]dodecylamine (Compound No. b-13)

6.0 g of 7,7,8,9,9-pentamethyl-3-(2,3-epoxypropyl)-2,4-dioxo-1,3,8-triazaspiro[4.5]decane and 1.8 g of dodecylamine were reacted and treated in a similar manner as described in Example 1, giving crude crystals. The crystals were recrystallized from a 5 : 1 by volume mixture of petroleum benzine and benzene, affording the desired compound in the form of white crystals melting at 186-187°C.

Example 21. 3-(2-Hydroxy-3-dodecylaminopropyl)-7,7,8,9,9-pentamethyl-2,4-dioxo-1,3,8-triazaspiro[4.5]decane (Compound No. a-12)

29.5 g of 7,7,8,9,9-pentamethyl-3-(2,3-epoxypropyl)-2,4-dioxo-1,3,8-triazaspiro[4.5]decane and 9.0 g of dodecylamine were reacted and treated in a similar manner as described in Example 1, giving crude crystals. The crystals were purified first by column chromatography through silica gel (eluent; ethyl acetate : benzene : ethanol : triethylamine = 20 : 4 : 2 : 1), then by recrystallization from n-hexane, affording the desired compound in the form of white crystals melting at 88-91°C.

Example 22. N,N-Bis[2-hydroxy-3-(7,7,8,9,9-pentamethyl-2,4-dioxo-1,3,8-triazaspiro[4.5]dec-3-yl)propyl]octylamine (Compound No. b-9)

29.5 g of 7,7,8,9,9-pentamethyl-3-(2,3-epoxypropyl)-2,4-dioxo-1,3,8-triazaspiro[4.5]decane and 6.8 g of octylamine were reacted and treated in a similar manner as described in Example 1, giving crude crystals. The crystals were recrystallized from ethanol, affording the desired compound in the form of white crystals melting at 188-190°C.

Example 23. N,N-Bis[2-hydroxy-3-(7,7,9,9-tetramethyl-2,4-dioxo-1,3,8-triazaspiro[4.5]dec-3-yl)propyl]dodecylamine (Compound No. b-12)

A mixture of 3.7 g of 7,7,9,9-tetramethyl-3-(2,3-epoxypropyl)-2,4-dioxo-1,3,8-triazaspiro[4.5]decane, 1.2 g of dodecylamine and 10 ml of octanol was heated at 100°C for 5 hours, under stirring. After completion of the reaction, the octanol was evaporated by distillation under reduced pressure. The resulting residue was purified by column chromatography through silica gel (eluent; benzene : ethyl acetate : triethylamine : ethanol = 12 : 12 : 3 : 1), dissolved in benzene. By adding a 1 : 1 by volume mixture of ethyl acetate and n-hexane, there was obtained the desired compound in the form of white crystals melting at 85-115°C.

Example 24.

A mixture of 100 parts of non-stabilized polypropylene powder (MFI-18), 0.2 part of stearyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate and 0.25 part of a stabilizer of

the present invention was kneaded homogeneously at 200°C for 10 minutes by means of a Brabender plastograph.The mass thus formed was compression-molded into a 2-3 mm thick sheet using a laboratory press.The sheet was then pressed at a pressure of 12 tons by a hydraulic press while heating at 260°C for 6 minutes,and then immediately poured into cold water to form a film of 0.5 mm thickness,from which a 0.1 mm thick film was prepared in a similar manner and cut into test specimens of 50 x 120 mm. The test specimens were exposed to the light at a black-pannel temperature of 63 ± 3°C in a Sunshine-Weather Meter and each of the test specimens was periodically examined to determine the percentage of elongation at break.The results of the tests were expressed by the ratio of the time until the elongation rate at break of the test specimens reached 50% of that at 0 hour of the test, and the time determined by the same way for the control specimens which were irradiated without adding a stabilizer of formula (I),as shown in Table 1.

Table I

Compound No.	Ratio	Compound No.	Ratio
a - 12	6.8	b - 30	5.1
21	7.5	31	5.3
b - 7	5.0	c - 1	6.1
9	5.7	17	5.2
11	6.1	d - 4	6.8
12	6.0	f - 6	4.7
13	7.7	13	4.2
19	6.7	14	5.9
20	6.0		

Example 25

To 100 parts of non-stabilized polystyrene pellets (Trade name: Styrone 666, product of Asahi-Dow Co.) was added 0.25 part of a stabilizer of the invention and the mixture was kneaded homogeneously at 200°C for 5 minutes by means of a Brabender plastograph. The mass thus prepared was immediately pressed into a plate of 2-3 mm thickness, which was further compression-molded at 180°C for 2 minutes into a 1.5 mm thick sheet. The sheets were irradiated at a black pannel temperature of 63 ± 3°C for 1500 hours in a BH-type Xenon-Weather-O-Meter (65 WR-type; 6500 watt lamp of the water-cooling type, supplied by Atlas Co.) according to method C specified under ASTM G26. The yellowness index was determined according to the ASTM 4 1925 method. The results obtained are shown in Table 2.

Table 2

Compound No.	YI_0	YI_{1500}
a - 21	1.8	8.3
b - 12	2.6	10.8
13	2.0	9.8
20	2.0	9.1
30	2.0	8.5
31	1.9	8.8
c - 17	2.2	9.4
d - 4	2.1	9.8
f - 13	2.2	9.5
No Addition	1.8	36.5

Example 26

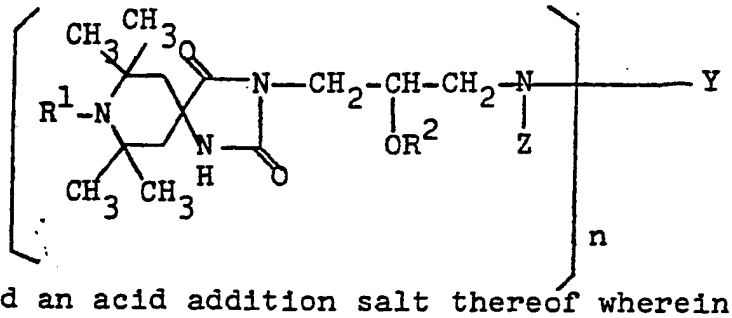
In 300 parts of dimethylformamide were homogeneously dissolved 100 parts of thermoplastic polyurethane (Trade name: Paraprene Pellet 22S, product of Nippon Polyurethane Kogyo Co.) and 0.25 part of a stabilizer of the invention, and the solution was spread on a glass plate to make a layer of about 0.4 mm thickness, which was dried at 60°C for 20 minutes and then at 120°C for 15 minutes to give a film of about 0.1 mm thickness. The film was irradiated at a black pannel temperature of 63 ± 3°C for 300 hours without water spray in a Sunshine Carbon Arc-Weather-Meter. The yellowness index was determined according to the ASTM D 1925 method. The results obtained are shown in Table 3.

Table 3

Compound No.	YI_0	YI_{300}
b - 12	1.8	21.3
13	1.6	21.3
20	2.2	23.8
30	2.1	23.0
31	1.9	25.1
d - 4	2.0	21.3
f - 13	2.0	23.6
No Addition	1.5	48.0

WHAT IS CLAIMED IS:

1. A piperidine-spiro-hydantoin derivative having the formula



(I)

and an acid addition salt thereof wherein

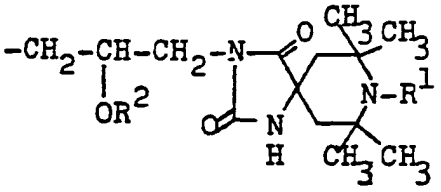
R^1 represents hydrogen or methyl,

R^2 represents hydrogen or an acyl group having not more than 18 C-atoms,

n is 1 or 2,

when n is 1,

Y and Z may be the same or different and represent hydrogen, an alkyl group having from 1-18 C-atoms, an alkenyl group having from 3-18 C-atoms, a cycloalkyl group having from 5-7 C-atoms, a phenyl group optionally substituted with methyl, an aralkyl group having 7 or 8 carbon atoms, a group of the formula $-CH_2-\underset{\underset{R^3}{|}}{CH}-OR^4$ (II) (wherein R^3 represents hydrogen or methyl and R^4 represents hydrogen or an acyl group having not more than 18 carbon atoms;) 2,2,6,6-tetramethyl-4-piperidyl or 1,2,2,6,6-pentamethyl-4-piperidyl or a group of the formula



(III),

or Y and Z may be joined together to form a tetramethylene, pentamethylene, 3-oxapentamethylene, succinyl, glutaryl, maleoyl or phthaloyl group or a group of the formula $-CH_2CH_2\rangle N-R^5$ wherein R^5 is a group of the formula (III), $-CH_2CH_2/$ with the proviso that R^2 and R^4 are hydrogen when Y and/or Z are hydrogen and that R^2 and R^4 are each hydrogen or an acyl group as defined or R^2 is hydrogen and R^4 is an acyl group as defined when Y and Z are both a group of the formula (II) or one of Y and Z is a group of the formula (II) and the other is different from hydrogen;

when n is 2,

Y represents an alkylene group having from 2-6 carbon atoms, a phenylene group which may be substituted by methyl, p-xylylene, 1,4-cyclohexylene, the 4,4'-diphenylether or 4,4'-diphenylmethane radical, 2,4-s-triazinediyl, 6-methyl- or 6-phenyl-2,4-s-triazinediyl, and

Z represents a group of the formula (III), 2,2,6,6-tetramethyl-4-piperidyl or 1,2,2,6,6-pentamethyl-4-piperidyl.

2. A compound as claimed in claim 1 wherein, when n is 1, Y and Z are the same or different and represent hydrogen, alkyl having from 1-18 carbon stoms, alkenyl having from 3-18 carbon atoms, cycloalkyl having from 5-7 carbon atoms, aralkyl having 7 or 8 carbon atoms, a group of the formula (II) or a group of the formula (III) with the proviso that, when Y and Z both represent alkyl, alkenyl, cycloalkyl, aralkyl or a group of the formula (II) as defined, said

groups are identical, and when n is 2, Y represents alkylene having from 2-6 carbon atoms, p-xylylene, 2,4-s-triazinediyl, 6-methyl- or 6-phenyl-2,4-s-triazinediyl, and Z represents a group of formula (III).

3. A compound as claimed in claim 2 wherein R^2 is hydrogen.

4. A compound as claimed in claim 2 wherein n is 1, R^2 is hydrogen, Y represents alkyl having from 1-18 carbon atoms, cyclohexyl or benzyl and Z represents hydrogen or a group of formula (III) wherein R^2 is hydrogen.

5. A compound as claimed in claim 4 wherein Z is a group of formula (III), and n, Y and R^2 have the same meaning as in claim 4.

6. A compound as claimed in claim 4 wherein Y represents alkyl having from 8-18 carbon atoms, Z represents a group of formula (III) and n and R^2 are as defined in claim 4.

7. A compound as claimed in claim 2 wherein n is 2, Y represents alkylene having from 2-6 carbon atoms, p-xylylene or 6-phenyl-2,4-s-triazinediyl, Z is a group of formula (III) and R^2 is hydrogen.

8. A compound as claimed in claim 2 wherein Y and/or Z represent a group of formula (III) or a group of formula (II) and R^2 and R^4 are the same or different and represent alkanoyl having not more than 18 carbon atoms, 3-(3,5-di-tert-butyl-4-hydroxyphenyl)-propionyl or benzoyl which may be substituted by an alkyl group having from 1-4

carbon atoms.

9. A compound as claimed in claim 1 wherein R^2 is hydrogen, Z represents a 2,2,6,6-tetramethyl-4-piperidyl or 1,2,2,6,6-pentamethyl-4-piperidyl group, n is 1 or 2, and Y, when n is 1, represents alkyl having from 1-18 carbon atoms and, when n is 2, Y represents alkylene having from 2-6 carbon atoms.

10. A synthetic polymer composition comprising a piperidine-spiro-hydantoin derivative of formula (I) or an acid addition salt thereof as claimed in claim 1,as stabilizer.

11. A synthetic polymer composition as claimed in claim 10 wherein the polymer is an olefin or diene polymer, a styrene polymer or polyurethane.

European Patent Office

EUROPEAN SEARCH REPORT

0006536
Application number

EP 79 101 929.2

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
P	DE - A1 - 2 757 105 (SANKYO) * claims 1, 9 *	1,10, 11
D	US - A - 3 941 744 (SANKYO) * claim 1 *	10,11
D	US - A - 3 975 462 (SANKYO) * claim 1 *	10,11
D,P	US - A - 4 097 587 (SANKYO et al.) * claim 4 *	10,11
A	DE - A1 - 2 625 967 (CIBA-GEIGY)	
D,A	US - A - 3 639 409 (SANKYO)	

CLASSIFICATION OF THE APPLICATION (Int. Cl.³)

C 07 D 471/10
C 08 K 5/34//
(C 07 D 471/10;
235/00, 221/00)

TECHNICAL FIELDS SEARCHED (Int.Cl.³)

C 07 D 471/10
C 08 K 5/34

CATEGORY OF CITED DOCUMENTS

X: particularly relevant
A: technological background
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P: intermediate document
T: theory or principle underlying the invention
E: conflicting application
D: document cited in the application
L: citation for other reasons

&: member of the same patent family, corresponding document

X The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Berlin	03-10-1979	FROELICH

EPO Form 1503.1 06.78